Conclusions

I. In this dissertation diffusion in polycrystalline materials was studied under conditions of short diffusion times and, as a consequence, high concentration gradients in the type-B kinetics. The conventional models were tested for such conditions against the calculated diffusion profiles, in order to estimate corresponding errors in the evaluation of the grain boundary (GB) diffusivities (D_{gb}) as well to develop improved evaluation procedures. It was found that:

1) The application of Le Claire's method (Eq. (1.16)) can lead to substantial errors, when applied to the calculated diffusion profiles.

2) One reason for the large errors is related to the nonlinearity of diffusion profiles in $\ln C_{av} = f(y^{6/5})$ plot, where C_{av} is the average concentration measured by one of the depth profiling methods and y is the penetration depth. An improved procedure is proposed for using Le Claire's relation:

Conclusions

a) The derivative of the diffusion profile should be plotted, in order to estimate the effect of profile nonlinearity.

b) The maximum value of the derivative should be used instead of fitting the profile to a straight line.

3) If Le Claire's method is to be applied, the derivative $\partial \ln C_{av}/\partial w^{6/5}$ should not be necessarily constant (w is the dimensionless coordinate) depending on the dimensionless parameter α (Eq. (1.9d)). Consequently, Le Claire's constant should be replaced by an improved value calculated by the following relation, giving the maximum value of $\partial \ln C_{av}/\partial w^{6/5}$ at fixed diffusion time:

$$\left(\frac{\partial \ln C_{av}}{\partial w^{6/5}} \right)_{max} = -0.77 - 0.71\alpha .$$

The dimensionless parameter α (Eq. (1.9d)) should be larger than 0.02, otherwise Le Claire's constant (≈ 0.78) may be safely used. This parameter can be easily estimated in the experiment, if the grain diffusivity (D_g) and the GB thickness (δ) are known.

4) For the dependence of the position of the maximum of the derivative $\partial \ln C_{av}/\partial y^{6/5}$ on the diffusion time the following empirical expression was found

$$y_{max}^{6/5} = K \cdot t^{H} ,$$

where H is around 0.60, K is a function of grain diffusivity (D_g) and D_{gb} and t the diffusion time. The expression requires the condition β > 10 (Eq. (1.9d)) to be fulfilled.

5) The maximum value of the derivative $\partial \ln C_{av}/\partial y^{6/5}$ can be found by using the following expression

$$\left| \frac{\partial \ln C_{av}}{\partial y^{6/5}} \right|_{max} = C \cdot \Delta^{F} \cdot t^{B} ,$$

where the ratio of diffusivities Δ equals D_{gb}/D_g, C depends on diffusion time and D_g, B and F are almost constants and given by –0.61 and –0.34, respectively.

II. The conventional models ignore the GBs orientations with respect to the diffusion direction. Realistic microcrystalline structures were used, in order to estimate these effects. For this purpose three general geometrical models were developed which are directly comparable with the popular model of square grains and parallel boundaries. It was observed that the relevant effects manifest themselves:

1) Steeper diffusion profiles with concentrations smaller than compared to the situation when only parallel GB diffusion paths are present. Consequently,

This increases the slope of the diffusion profile with decreasing grain sizes, and, as a result of this, the use of Le Claire's relation underestimates D_{gb}.

2) General geometries with similar numbers of perpendicular and parallel paths are very well comparable with the model of square grains. Consequently,

This makes the model of square grains as a good approximation of the polycrystalline microstructure also for instationary diffusion.

3) Negligible role of perpendicular GB diffusion paths in the model of square grains, if the diffusion time increase guarantees the A-regime of diffusion. Consequently,

It was observed that the concentration profiles in both the model of parallel boundaries and the model of square grains almost coincide at very long diffusion times.

Additionally, the effects of impurity segregation were taken into account when analyzing diffusion in realistic microstructures. Very small and very large segregation coefficients (s) were used, allowing the conventional equations to be compared for different situations. The following conclusions were made:

1) The Hart-Mortlock (Eq. (1.17b)) equation is not valid when deducing D_{gb} with s larger than 20 even in the model of parallel boundaries. The use of this equation gives increasing errors with s. For example, errors of the order of 90% can be observed for s = 160 – 640.

Conclusions

2) The Hart-Mortlock equation is correct for finding D_{gb} in the model of square grains, if the volume (area) fraction of GBs is taken as it is in the model of parallel boundaries, and segregation is negligible. This conclusion refers to the negligible role of perpendicular GB diffusion paths at long diffusion times.

3) The Maxwell-Garnett type equation (Eq. (1.18b)) for segregation is not valid in the model of parallel boundaries under conditions of strong segregations and may be only applied in the model of square grains. Consequently,

Inappropriate use of the Maxwell-Garnett type equation increases the errors of finding D_{gb}. The error increases with s and can reach 90% and larger for s ≥ 640.

III. The existence of depleted space charge layers (SCL) in ionic materials was taken into account. A special model was proposed in which constant space charge layer diffusivity (D_{scl}) is introduced. The diffusion profiles were simulated by the finite element method in the B- as well as A-regime varying the ratio $\Lambda = D_g/D_{scl}$. The main results are summarized in the following:

1) The depleted space charge layer leads to diffusion profiles with slopes different from those without space charge layers. Namely, the slope of the profile decreases with the ratio $\Lambda = D_g/D_{scl}$. Consequently,

The conventional Le Claire relation (Eq. (1.16)) overestimates D_{gb} by a factor of 6, if $\Lambda = 10^3$ at very short diffusion times.

2) The maximum of the derivative of the profile measured in the B-regime is determined by the transport process between the GB and SCL. Using the new equation for the maximum (Eq. (2.7) or I.5) of the derivative allows the ratio D_{gb}/D_{scl} to be obtained and, as a result of this, D_{gb} according to modified original Le Claire's relation (Eq. (1.14))

$$D_{gb,app} = \frac{4}{\left(D_{gb}/D_{scl}\right)t\delta^2}\left(-\frac{\partial \ln C_{av}}{\partial w^{6/5}}\right)^{10/3}\left(-\frac{\partial \ln C_{av}}{\partial y^{6/5}}\right)^{-10/3},$$

where $\partial \ln C_{av}/\partial w^{6/5}$ is determined by Eq. (1.14) or is -0.78 depending on α (see also I.3).

3) The kinetic regimes are shifted in time if the blocking space charge effects play a role. In this case, the diffusion profiles should be plotted in nonlinear scale according to $\ln C_{av} = f(y^{6/5})$ even if the nominal A-regime conditions are satisfied, in order to qualitatively estimate the effect of blocking SCLs. Consequently,

In the nominal A-regime strongly blocking SCLs may lead to a severe underestimation of D_{gb} by using a conventional analysis.

4) The role of perpendicular GB paths increases, if these are surrounded by blocking space charge regions. Consequently,

a) Crossing GBs with SCLs lead to the drop and significant decrease of concentration in the model of square grains.

b) Crossing GBs (square grains) with SCLs lead to further blocking effects and even for long diffusion times (nominal A-regime) modified profiles with two distinguishable parts and varying slopes may result.

IV. Moreover, along with the computer calculations, a procedure was developed for proper simulations of diffusion in polycrystalline materials by means of the finite element method. The procedure considers simulation of diffusion in a semi-infinite solid and the main aspects are summarized as follows:

1) Simulating diffusion in the B-regime, a special attention should be paid to the finite element mesh. Consequently,

a) The derivatives of diffusion profiles can be calculated for different mesh densities, in order to find the optimal mesh with respect to the initial time and the diffusion times of interest.

b) The denser mesh the shorter diffusion times for which profiles can be obtained.

2) The derivatives allow one also to estimate the effect of the boundary at the bottom of the geometrical model (sample) used, e.g., the condition of zero flux. Consequently,

If the maximum of the profile is not distinguishable, the length of the geometrical model should be increased and, if necessary, the density of mesh should be decreased.

3) The length of the geometrical model should be at least $4\sqrt{D_{eff}t}$ (D_{eff} is the effective diffusivity which reflects the homogeneous character of diffusion in the A-regime and can be obtained by using the Hart or Maxwell-Garnett equation) for properly simulating the diffusion profiles in the A-regime, otherwise the effect of the boundary condition becomes significant.

4) The simulation mesh density in the A-regime can be significantly reduced in comparison with the B-regime. However, the time increment can be increased. It means that some adaptive procedure with respect to the time increment is useful when simulating the diffusion profiles in the B-regime and A-regime simultaneously.